

Sr)TiO₃), and the like are investigated as a capacitor material. As electrode materials of these capacitors, noble metal thin films of ruthenium, platinum, iridium, and the like, or oxide thin films of these noble metals become necessary. In particular, iridium and iridium oxide are watched as a leading part of electrode materials in the future. As the production process of iridium and iridium oxide thin films, a sputtering process and a chemical vapor deposition process (CVD process) are employed. In particular, the CVD process is being considered as the main current in the production process of thin film electrodes in the future. This is because not only it is easy to produce uniform films, but also the step coverage is excellent, and therefore, this process can cope with higher density against the recent circuits and electronic parts.

[0003]

As the precursor for forming thin films using this CVD process, it is considered that among metallic compounds, organometallic compounds that are low in melting point and easy in handling are suitable. Hitherto, tris(dipivaloylmethanato)iridium, tris(acetylacetonato)iridium, cyclopentadienyl(1,5-octadiene)iridium, and the like have been investigated as an organometallic compound for the purpose of depositing an iridium or iridium oxide thin film. These iridium compounds are high in stability in the atmosphere and non-toxic, and therefore, have aptitude as a precursor of CVD. However, these iridium compounds are solid at the ambient temperature and involve such a problem that vaporization of the precursor and transportation to a substrate are difficult.

[0004]

In recent years, iridium compounds having a low melting point are being eagerly investigated. As a measure of making the organometallic iridium compounds have a low melting point, there is employed a compound in which at least one hydrogen atom on a

cyclopentadiene ring is substituted with a lower alkyl group such as a methyl group and an ethyl group. For example, as cyclopentadiene derivatives, ethylcyclopentadienyl(1,5-cyclooctadiene)iridium is disclosed (for example, see Patent Document 1). Since this organometallic compound is liquid at the ambient temperature, and its melting point is low as compared with that of cyclopentadienyl(1,5-cyclooctadiene)iridium, it is considered that this compound is possessed of characteristics necessary as the precursor to be applied to the CVD process. However, this compound has extremely high stability, and the decomposition temperature of the complex is high. Accordingly, it is inevitably required to increase the substrate temperature at the time of film formation. Also, there is encountered such a problem that an iridium oxide film is hardly formed.

[0005]

On the other hand, cyclopentadienyl(cyclohexadiene)iridium and cyclopentadienyl(butadiene)iridium are solid at the ambient temperature, too and therefore, involve problems in vaporization of the precursor and transportation to a substrate (for example, non-patent document). There has not been made any report of synthesis of iridium complexes that are liquid at the ambient temperature and have excellent vaporization characteristic.

[0006]

Patent Document 1

JP-A-11-292888

Non-Patent Document 1

B.F.G. Johnson, J. Lewis, and D.J. Yarrow, *J. C. S. Dalton*, 2084 (1972) and L.A. ORO, *Inorg. Chem. Acta*, **21**, L6 (1977)

[0007]

[Problems that the Invention is to Solve]

The present invention has been made in view of the above technical problems. That is, the present invention has an object to provide an organometallic compound for forming a thin film comprising iridium or iridium oxide on a substrate by the CVD process, the organometallic compound having a low melting point, excellent vaporization characteristic and low film formation temperature.

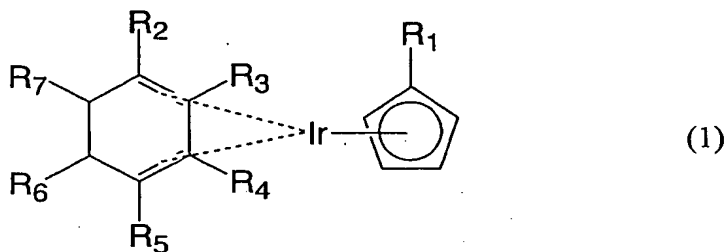
[0008]

The present inventors have made extensive and intensive investigations to overcome the above-described problems. As a result, it has been found that the decomposition temperature can be decreased by introducing a lower alkyl group into a cyclopentadienyl ring of cyclopentadienyl(cyclohexadiene)iridium which is one of cyclopentadiene derivatives. This finding led development of a novel iridium compound exhibiting a melting point such that it is liquid at the ambient temperature and having good vaporization characteristic and decomposition characteristic, that is, a novel iridium compound having one cyclopentadiene derivative bonded thereto, and one cyclohexadiene derivative coordinated thereto.

[0009]

The present invention provides an organometallic iridium compound represented by the following general formula (1):

[0010]



[0011]

wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are the same or different and each represents hydrogen, a halogen, a lower acyl group, a lower alkoxy group, a lower alkoxycarbonyl group, or a lower alkyl group, provided that the case where all of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 represent hydrogen is excluded. The present invention is described in more detail below.

[0012]

Definition of the terms used in the present specification and specific examples thereof will be described. The term "lower" as referred to in the present specification and claims means one containing a linear, branched or cyclic hydrocarbon group having 1-6 carbon atoms in the group given this term, unless otherwise indicated.

[0013]

Therefore, examples of the lower alkyl group used in R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , or R_7 include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl (amyl) group, an isopentyl group, a neopentyl group, a tert-pentyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 1,2-dimethylpropyl group, a hexyl group, an isohexyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl group, a 1,1-dimethylbutyl group, a 2,2-dimethylbutyl group, a 1,3-dimethylbutyl group, a 2,3-dimethylbutyl group, a 3,3-dimethylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1,1,2-trimethylpropyl group, a 1,2,2-trimethylpropyl group, a 1-ethyl-1-methylpropyl group, a 1-ethyl-2-methylpropyl group, a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cyclopropylmethyl group, a cyclopropylethyl group, and a cyclobutylmethyl group. Of those, a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group are preferable.

[0014]

Examples of the lower alkoxy group used in R₁, R₂, R₃, R₄, R₅, R₆, or R₇ include a methoxy group, an ethoxy group, a propoxy group, an isopropoxy group, a butoxy group, an isobutoxy group, a sec-butoxy group, a tert-butoxy group, a pentyloxy group, a 1-methylbutyloxy group, a 2-methylbutyloxy group, a 3-methylbutyloxy group, a 1,2-dimethylpropyloxy group, a hexyloxy group, a 1-methylpentyloxy group, a 1-ethylpropyloxy group, a 2-methylpentyloxy group, a 3-methylpentyloxy group, a 4-methylpentyloxy group, a 1,2-dimethylbutyloxy group, a 1,3-dimethylbutyloxy group, a 2,3-dimethylbutyloxy group, a 1,1-dimethylbutyloxy group, a 2,2-dimethylbutyloxy group, and a 3,3-dimethylbutyloxy group. Of those, a methoxy group, an ethoxy group, and a propoxy group are preferable.

[0015]

Examples of the lower alkoxycarbonyl group used in R₁, R₂, R₃, R₄, R₅, R₆, or R₇ include a methoxycarbonyl group, an ethoxycarbonyl group, a propoxycarbonyl group, an isopropoxycarbonyl group, a cyclopropoxycarbonyl group, a butoxycarbonyl group, an isobutoxycarbonyl group, a sec-butoxycarbonyl group, and a tert-butoxycarbonyl group. Of those, a methoxycarbonyl group, an ethoxycarbonyl group, a propoxycarbonyl group, an isopropoxycarbonyl group, and a cyclopropoxycarbonyl group are preferable.

[0016]

Examples of the lower acyl group used in R₁, R₂, R₃, R₄, R₅, R₆, or R₇ include a formyl group, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, a 1-methylpropylcarbonyl group, an isovaleryl group, a pentylcarbonyl group, a 1-methylbutylcarbonyl group, a 2-methylbutylcarbonyl group, a 3-methylbutylcarbonyl group, a 1-ethylpropylcarbonyl group, and a

2-ethylpropylcarbonyl group. Of those, a formyl group, an acetyl group, and a propionyl group are preferable.

[0017]

In addition to the above lower alkyl group, lower alkoxy group, lower alkoxycarbonyl group and lower acyl group, a hydrogen atom or a halogen atom is preferably used for R₁, R₂, R₃, R₄, R₅, R₆, or R₇, which are the same or different. Specific examples of the halogen atom include fluorine, chlorine, bromine, and iodine. Of those, fluorine and chlorine are preferable.

[0018]

Although examples of R₁ to R₇ are enumerated above, R₁ to R₇ each preferably represents hydrogen or a lower alkyl group, and more preferably hydrogen or a lower alkyl group having 1-3 carbon atoms. Specific compound represented by the general formula (1) is (ethylcyclopentadienyl)(1,3-cyclohexadiene)iridium.

[0019]

Production method of the iridium compound represented by the general formula (1) is not particularly limited. For example, the objective product can be prepared by stirring the iridium compound which is an iridium source, the cyclohexadiene derivative in excess to iridium, and the cyclopentadiene derivative in an appropriate solvent, and reacting under appropriate conditions. For example, the iridium compound which is an iridium source is reacted with the cyclohexadiene derivative, and the resulting reaction product is then reacted with the cyclopentadiene derivative. A post treatment is not particularly limited. However, as a general method, the reaction mixture after completion of the reaction is concentrated; the desired compound is extracted from the resulting mixture using an organic solvent such as pentane, hexane or ether; and the extract is subjected to column chromatography using alumina as a carrier and an

appropriate organic solvent as an eluant, whereby the desired iridium compound of the present invention can be obtained.

[0020]

[Example]

The present invention is described in more detail by reference to the Examples, but it should be understood that the invention is not construed as being limited thereto.

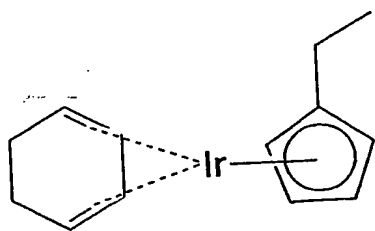
[0021]

EXAMPLE 1

Synthesis and thermal decomposition characteristic of (ethylcyclopentadienyl)(1,3-cyclohexadiene)iridium:

0.5 g of chlorobis(1,3-cyclohexadiene)iridium was added to 10 ml of THF, and a reaction flask was cooled to -78°C , to which was then added 20 ml of a THF solution of 0.18 g of lithium ethylcyclopentadienide. The resulting mixture was stirred at -78°C for 30 minutes, the temperature was then raised to room temperature step by step, and the resulting mixture was further allowed to react for 17.5 hours, followed by concentration to obtain a muddy mixture. The muddy mixture was subjected to extraction with hexane, and the extract solution was subjected to column chromatography (eluant: hexane) using alumina to obtain 145 mg of desired (ethylcyclopentadienyl)(1,3-cyclohexadiene)iridium.

[0022]



[0023]

¹H-NMR (500 MHz, CDCl₃, δ ppm):

5.12 (t, J = 2.0 Hz, 2H), 5.02 (t, J = 2.0 Hz, 2H), 4.90 (m, 2H), 3.32 to 3.37 (m, 2H), 2.40 (q, J = 7.5 Hz, 2H), 1.39 to 1.47 (m, 2H), 1.25 to 1.29 (m, 2H), 1.11 (t, J = 7.5 Hz, 3H).

IR (neat, cm⁻¹):

810, 1000, 1170, 1315, 1460, 2925

MS (GC/MS, EI):

Molecular ion peak of (ethylcyclopentadienyl)(1,3-cyclohexadiene)iridium in terms of ¹⁹³Ir: m/z 362

Orange oily material

[0024]

Decomposition Characteristic

With respect to the resulting (ethylcyclopentadienyl)(1,3-cyclohexadiene)iridium, the thermal decomposition characteristic was examined in the following manner.

Analysis condition of decomposition characteristic:

Analysis method: Power compensation differential scanning calorimetry (DSC)

Analysis condition:

Reference: Alumina

Inert gas: Nitrogen, 50 ml/min

Temperature rising: 10°C/min

The results obtained are shown in Fig. 1. It is apparent from Fig. 1 that in the iridium compound of the present invention, the decomposition temperature is shifted to the low temperature side as compared with that in Comparative Example described hereinafter.

[0025]

COMPARATIVE EXAMPLE 1

Decomposition characteristic of ethylcyclopentadienyl(1,5-cyclooctadiene)iridium:

With respect to ethylcyclopentadienyl(1,5-cyclooctadiene)iridium as a known compound, the decomposition characteristic was examined in the same manner as in Example 1. The results obtained are shown in Fig. 2. It is apparent from Fig. 2 that in this known compound, the decomposition temperature was located in the high temperature side as compared with those of the compounds of the present invention described in Example 1.

[0026]

[Advantage of the Invention]

The iridium compounds of the present invention is liquid at room temperature, and where used as the CVD precursor, it can be quantitatively supplied by gas bubbling. Further, since the compound can be thermally decomposed at low temperatures as compared with the conventional materials, it is possible to form an Ir-containing thin film having excellent step coverage on a substrate. In this way, it is possible to form an Ir-containing thin film from the iridium compound of the present invention by the CVD process having excellent mass productivity.

[Brief Description of the Drawings]

Fig. 1 is a view showing a DSC curve obtained in Example 1.

Fig. 2 is a view showing a DSC curve obtained in Comparative Example 1.